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Specification

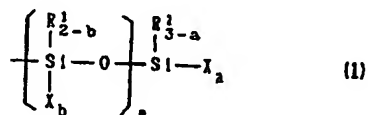
1. Title of the Invention

A curable composition

2. Scope of Claims

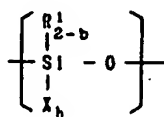
1. A curable composition which contains (a) a saturated hydrocarbon polymer having at least one silicon-containing group which possesses hydroxy or hydrolyzable groups bonded to a silicon atom, and which can crosslink by forming siloxane bonds, and (b) a saturated hydrocarbon oligomer.

2. A composition according to Claim 1 where the aforesaid silicon-containing group is a group represented by general formula (1):



(where, in the formula, R^1 and R^2 are each a C_{1-20} alkyl group, C_{6-20} aryl group, C_{7-20} aralkyl group or a triorganosiloxane group represented by $(R')_3SiO-$ (where R' is a C_{1-20} monovalent hydrocarbon group, and the three

R¹ groups may be the same or different), and where two or more of R¹ or R² are present, these may be the same or different, and X is a hydroxy group or a hydrolyzable group, and when there are two or more thereof present then these may be the same or different, a is 0, 1, 2 or 3, b is 0, 1 or 2, but a + mb ≥ 1, and there is no need for b in the m x



moieties to be the same, and m is 0 or an integer in the range 1 to 19).

3. A composition according to Claim 2 where X in general formula (1) is a hydrogen atom, hydroxy group, alkoxy group, acyloxy group, ketoximato group, amino group, amido group, aminooxy group, mercapto group or alkenyloxy group, and when there are two or more of X present then these may be the same or different.

4. A composition according to Claim 2 where X in general formula (1) is an alkoxy group.

5. A composition according to Claim 1 where the aforesaid saturated hydrocarbon polymer is an isobutylene polymer or a hydrogenated polybutadiene polymer.

6. A composition according to Claim 5 where the number average molecular weight of the aforesaid isobutylene polymer or hydrogenated polybutadiene polymer is 500 to 30,000.

7. A composition according to Claim 1 where the added amount of saturated hydrocarbon oligomer lies in the range from 1 to 1000 parts by weight per 100 parts by weight of the aforesaid saturated hydrocarbon polymer.

3. Detailed Description of the Invention

[Industrial Field of Application]

The present invention relates to a curable composition which contains a saturated hydrocarbon polymer having at least one silicon-containing group (sometimes referred to below as a reactive silicon group) which possesses hydroxy or hydrolyzable groups bonded to a silicon atom, and which can crosslink by forming siloxane bonds, together with a saturated hydrocarbon oligomer.

[Prior-Art and Problem to be Resolved by the Invention]

Polyalkylene oxide polymers which have a reactive silicon group at the molecular terminals are already known and are used in considerable quantities. They possess the interesting property of being cured by moisture at room temperature, with a rubbery cured material being obtained. However, the heat resistance, water resistance and weather resistance, etc, of such polymers are inadequate and so their applications are restricted.

As a method for resolving such difficulties, saturated hydrocarbon polymers, such as polyisobutylene, having a reactive silicon group at the molecular terminals have been investigated (see, for example, Japanese Patent Application No. 61-148895). However, while the heat resistance, water resistance and weather resistance, etc,

of this polymer are considerably improved when compared to the polyalkylene oxide polymers, it is necessary to have a long molecular chain in order for the cured material to have good rubber elasticity, so that there is the disadvantage that the viscosity of the composition is inevitably high and handling difficult, and hence from the point of view of practical employment applications are restricted.

[Means for Resolving the Problem]

The present invention has the objective of overcoming the disadvantages possessed by the curable composition containing a saturated hydrocarbon polymer which possesses reactive silicon groups as described above, and of obtaining a composition which is rapidly cured by the moisture in air at room temperature and which, while maintaining the properties provided by a saturated hydrocarbon polymer such as heat resistance, water resistance and weather resistance, etc, is also a composition of low viscosity and excellent usability. Specifically, it relates to a curable composition containing

- (a) a saturated hydrocarbon polymer having at least one silicon-containing group which possesses hydroxy or hydrolyzable groups bonded to a silicon atom, and which can crosslink by forming siloxane bonds, and
- (b) a saturated hydrocarbon oligomer.

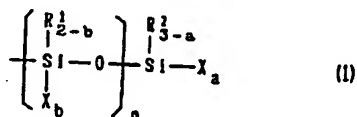
The cured product of the composition of the present invention has outstanding heat resistance, water resistance and weather resistance, etc, and furthermore the usability of the composition is excellent. When

compared to the cured product of a composition which does not contain the (b) component saturated hydrocarbon oligomer, the cured product of the composition of the present invention has high strength and high elongation (low elastic modulus). Moreover, the cured product of this composition is outstanding in its adhesion properties and, furthermore, it is characterized by the fact that there is little bleeding of component (b) from the cured product, and in the case where the surface of the cured product is painted there is no contamination of the painted material.

[Practical Embodiments]

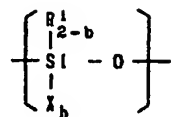
In the present invention, as the (a) component there is used a saturated hydrocarbon polymer having at least one silicon-containing group which possesses hydroxy or hydrolyzable groups bonded to a silicon atom, and which can crosslink by forming siloxane bonds, that is to say a reactive silicon group.

Typical examples of this reactive silicon group are the groups represented by general formula (1):



(where, in the formula, R^1 and R^2 are each a C_{1-20} alkyl group, C_{6-20} aryl group, C_{7-20} aralkyl group or a triorganosiloxane group represented by $(R')_3SiO-$ (where R' is a C_{1-20} monovalent hydrocarbon group, and the three R' groups may be the same or different), and where two or more of R^1 or R^2 are present, these may be the same or different, and X is a hydroxy group or a hydrolyzable

group, and when there are two or more thereof then these may be the same or different, a is 0, 1, 2 or 3, b is 0, 1 or 2, but $a + mb \geq 1$, and there is no need for b in the $m \times$

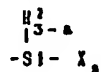


moieties to be the same, and m is 0 or an integer in the range 1 to 19).

Specific examples of the aforesaid hydrolyzable group are hydrogen atom, alkoxy group, acyloxy group, ketoximato group, amino group, amido group, aminooxy group, mercapto group, alkenyloxy group and other such generally-used groups. Of these, alkoxy groups are particularly preferred in that the hydrolysis is mild and handling is easy.

From one to three such hydrolyzable groups and/or hydroxy groups can be bonded to one silicon atom, and it is preferred that $(a + mb)$ lies within the range 1 to 5. In the case where two or more hydrolyzable groups and/or hydroxy groups are bonded within a reactive silicon group, these may be same or different.

The silicon atom forming the aforesaid reactive silicon group may be a single such silicon atom or there may be two or more, but in the case of silicon atoms linked by means of for example siloxane bonds, up to 20 are preferred. In particular, the reactive silicon groups represented by the formula:



(where R^2 , X and a have the same meanings as above) are readily available, so are preferred.

At least one, and preferably 1.1 to 5 reactive silicon groups are present in a single molecule of the saturated hydrocarbon polymer. If the number of reactive silicon groups contained in the molecule is less than one, then the curability is inadequate and it becomes difficult to manifest good rubber elastic behaviour.

The reactive silicon groups may be present at the ends of the molecular chains of the saturated hydrocarbon polymer, or within the molecules, or both. In particular, in the case where the reactive silicon groups are present at the molecular chain terminals, the proportion of saturated hydrocarbon polymer component contained in the finally-formed cured material which constitutes effective network chains will be higher, so this is preferred in terms of the ease of obtaining a rubbery cured material of high strength and high elongation. Again, there may be used one such saturated hydrocarbon polymer with reactive silicon groups, or two or more types may be jointly employed.

The polymer which forms the skeletal structure of the saturated hydrocarbon polymer with reactive silicon groups used in the present invention can be obtained by methods such as

(1) the polymerization of monomer chiefly comprising ethylene, propylene, 1-butene, isoprene or other such olefin compound with from 1 to 6 carbons, or

(2) the homopolymerization of butadiene, isoprene or other such diene compound or the copolymerization of an

aforesaid olefin compound and a diene compound, followed by hydrogenation,

but in terms of the ease of introduction of functional groups at the terminals, in terms of the ease of molecular weight control and in terms of being able to increase the number of terminal functional groups, it is preferred that there be used isobutylene polymer or hydrogenated polybutadiene polymer.

Now, in this specification, the concept of a saturated hydrocarbon polymer means a polymer which substantially does not contain carbon-carbon unsaturated bonds other than in an aromatic ring.

The aforementioned isobutylene polymer may be one in which all the monomer units are formed from isobutylene or, alternatively, the isobutylene polymer may also contain units from monomers which are copolymerizable with isobutylene but preferably no more than 50% (wt%, so too below), more preferably no more than 30%, and in particular no more than 10% thereof.

Examples of these monomer components are C₄₋₁₂ olefins, vinyl ethers, aromatic vinyl compounds, vinyl silanes, allyl silanes or the like. Specific examples of such copolymer components are 1-butene, 2-butene, 2-methyl-1-butene, 3-methyl-1-butene, pentene, 4-methyl-1-pentene, hexene, vinyl cyclohexane, methyl vinyl ether, ethyl vinyl ether, isobutyl vinyl ether, styrene, α -methylstyrene, dimethylstyrene, monochlorostyrene, dichlorostyrene, β -pinene, indene, vinyltrichlorosilane, vinylmethyldichlorosilane, vinyl dimethylchlorosilane, vinyl dimethylmethoxysilane, vinyltrimethylsilane,

divinyldichlorosilane, divinyldimethoxysilane, divinyl-
dimethylsilane, 1,3-divinyl-1,1,3,3-tetramethyl-
disiloxane, trivinylmethylsilane, tetravinylsilane,
allyltrichlorosilane, allylmethyldichlorosilane,
allyldimethylchlorosilane, allyldimethylmethoxysilane,
allyltrimethylsilane, diallyldichlorosilane,
diallyldimethoxysilane, diallyldimethylsilane, γ -
methacryloyloxypropyltrimethoxysilane, γ -
methacryloyloxypropylmethyldimethoxysilane and the like.

When a vinylsilane or an allylsilane is used as an aforesaid monomer copolymerizable with isobutylene, the silicon content of the polymer is increased, there are more groups which can act as a silane coupling agent and the adhesion properties of the composition obtained are enhanced.

In the same way as for the isobutylene polymer above, there may also be included other monomer units besides the monomer units which constitute the chief component in the case of the aforesaid hydrogenated polybutadiene polymer or in the case of other saturated hydrocarbon polymers.

Furthermore, in the saturated hydrocarbon polymer used in the present invention, there may also be included a small amount of monomer units such as those from a polyene compound like butadiene or isoprene, which leave a double bond present following polymerization, providing the amount of these monomer units lies within a range such that the objectives of the present invention are still realized, preferably no more than 10%, more preferably no more than 5% and in particular no more than 1%.

The number average molecular weight of the aforesaid saturated hydrocarbon polymer, and preferably of the isobutylene polymer or hydrogenated butadiene polymer, is desirably within the range about 500 to 30,000, and in particular within the range about 1,000 to 15,000, from the point of view of the ease of handling of the liquid material.

Next, explanation is provided on the method of producing the saturated hydrocarbon polymer with reactive silicon groups.

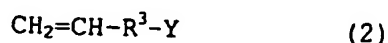
Of the aforementioned isobutylene polymers with reactive silicon groups, the isobutylene polymers with reactive silicon groups at the terminals of the molecular chains can be produced using an isobutylene polymer having terminal functional groups, and preferably having all terminal functional groups, obtained by the polymerization method referred to as the Inifer method (a cationic polymerization method which employs a specified compound referred to as an 'inifer' which functions jointly as an initiator and chain transfer agent). This method of polymerization is described in, for example, the specifications of Japanese Patent Application Nos 61-148895, 61-150088, 62-90078, 62-179733 and 62-194838.

Furthermore, isobutylene polymers with reactive silicon groups within the interior of the polymer chain may be produced by performing copolymerization by the addition, to the monomer chiefly comprising isobutylene, of a vinylsilane or an allylsilane which possesses a reactive silicon group.

If, when producing an isobutylene polymer which has reactive silicon groups at the molecular chain terminals, there is first carried out the copolymerization, with the isobutylene monomer chief component, of a vinylsilane or an allylsilane which possesses a reactive silicon group, after which the reactive silicon groups are then introduced at the terminals, there may be produced an isobutylene polymer with reactive silicon groups at the terminals and within the polymer chains.

Specific examples of the aforesaid vinylsilane or allylsilane with a reactive silicon group are vinyltrichlorosilane, vinylmethyldichlorosilane, vinyl-dimethylchlorosilane, vinyl-dimethylmethoxysilane, divinyl-dichlorosilane, divinyl-dimethoxysilane, allyltrichlorosilane, allylmethyldichlorosilane, allyl-dimethylchlorosilane, allyl-dimethylmethoxysilane, diallyldichlorosilane, diallyldimethoxysilane, γ -methacryloyloxypropyltrimethoxysilane, γ -methacryloyloxypropylmethyldimethoxysilane and the like.

The corresponding hydrogenated polybutadiene polymer may be produced for example by first of all converting the hydroxy groups of a hydroxy-terminated hydrogenated polybutadiene polymer to oxymetal groups such -ONa or -OK after which, by the reaction of an organic halogen compound represented by general formula (2):



(where Y represents a chlorine atom, iodine atom or other halogen atom, and R^3 is preferably a divalent group selected from $-\text{R}^4-$, $-\text{R}^4-\text{O}-\text{CO}-$ or $-\text{R}^4-\text{CO}-$ [where R^4

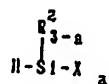
represents a divalent hydrocarbon group with 1 to 20 carbons, preferably specifically an alkylene group, cycloalkylene group, arylene group or aralkylene group], $-\text{CH}_2-$ and $-\text{R}''-\text{C}_6\text{H}_4-\text{CH}_2-$ [where R'' is a C_{1-10} hydrocarbon group], there is produced a hydrogenated polybutadiene polymer with terminal olefin groups (hereinafter this is referred to as an olefin-terminated hydrogenated polybutadiene polymer).

Examples of the method for converting the terminal hydroxy groups of a hydroxy-terminated hydrogenated polybutadiene polymer to oxymetal groups are by reaction with an alkali metal such as Na or K; a metal hydride such as NaH ; a metal alkoxide such as NaOCH_3 ; or a caustic alkali such as caustic soda or caustic potash.

In the aforesaid method, an olefin-terminated hydrogenated polybutadiene polymer having roughly the same molecular weight as the hydroxy-terminated hydrogenated polybutadiene polymer used as the starting material is obtained. However, in the case where a polymer of still higher molecular weight is desired, it is possible to increase the molecular weight by reaction with an organic polyhalide compound containing two or more halogen atoms in the molecule, such as methylene chloride, bis(chloromethyl)benzene or bis(chloromethyl) ether, prior to the reaction with the organic halogen compound of general formula (2), after which reaction is then performed with the organic halogen compound of general formula (2) and, in this way, there can be obtained a higher molecular weight hydrogenated polybutadiene polymer with terminal olefin groups.

Specific examples of the organic halogen compounds represented by general formula (2) above are allyl chloride, allyl bromide, vinyl(chloromethyl)benzene, allyl(chloromethyl)benzene, allyl(bromomethyl)benzene, allyl (chloromethyl) ether, allyl(chloromethoxy)benzene, 1-butenyl (chloromethyl) ether, 1-hexenyl-(chloromethoxy)benzene, allyloxy(chloromethyl)benzene and the like. However, there is no restriction to the examples given. Amongst the examples, allyl chloride is preferred in that it is cheap and easily reacted.

With regard to the introduction of the reactive silicon groups into the aforesaid olefin-terminated hydrogenated polybutadiene polymer, just as in the case of the isobutylene polymer with reactive silicon groups at the molecular terminals, production can be carried out for example by the addition reaction of a hydrosilane compound having a hydrogen atom bonded to the group represented by general formula (1), preferably a compound represented by the general formula



(where R^2 , X and a have the same meanings as above), using a platinum catalyst.

Specific examples of the hydrosilane compound comprising a hydrogen atom bonded to the group represented by aforesaid general formula (1) are halo-silanes such as trichlorosilane, methylchlorosilane, dimethylchlorosilane and phenylchlorosilane; methyldichlorosilane, phenyldichlorosilane; alkoxy-silanes such as trimethoxysilane, triethoxysilane, methyldiethoxysilane, methyldimethoxysilane and phenyldimethoxysilane; acyloxy-silanes such as methyldiacetoxysilane and phenyldiacetoxysilane; and

ketoxyatosilanes such as bis(dimethylketoximato)-methylsilane and bis(cyclohexylketoximato)methylsilane. However, there is no restriction to these examples. Amongst the examples given, the halosilanes and alkoxysilanes are particularly preferred.

While the (a) component provides a rubbery cured material which has excellent water resistance, heat resistance and weather resistance, etc, it is of high viscosity and difficult to handle, so in order to reduce the viscosity of the (a) component and make it easier to handle, and in order to enhance the elongation properties of the cured material while maintaining or enhancing the strength, in the present invention there is employed the (b) component saturated hydrocarbon oligomer.

This saturated hydrocarbon oligomer has a structure resembling that of the main chain of the (a) component, and it is excellent in its water resistance, heat resistance and weather resistance, etc. Furthermore, its compatibility with the (a) component is excellent and it may be mixed therewith in any proportions. In addition, it possesses the characteristic of not readily bleeding out.

There are no particular restrictions on the molecular weight of this oligomer, but it is preferably in the range 100 to 20,000, and more preferably in the range 100 to 2,000. It will not contain unsaturated carbon-carbon bonds other than those in an aromatic ring, but it may contain halogen atoms, aromatic rings and alicyclic groups.

Specific examples of such oligomers are polyvinyl oligomers such as polybutene, hydrogenated polybutene, ethylene/ α -olefin oligomer, atactic propylene and α -methylstyrene oligomer; aromatic oligomers such as biphenyl, triphenyl and the like; hydrogenated poly-ene oligomers such as hydrogenated liquid polybutadiene; paraffinic oligomers such as paraffin oil and chloroparaffins, etc; and cycloparaffin oligomers such as naphthene oils. In the case where there is used a polymer without aromatic rings, such as polyisoprene or hydrogenated polybutadiene, as the (a) component polymer, it is preferred that there be used a hydrocarbon oligomer which substantially does not contain carbon-carbon unsaturated bonds such as aromatic-ring-free hydrogenated polybutene, hydrogenated liquid polybutadiene, paraffin oil, chloroparaffin oil, naphthene oil, atactic polypropylene or the like. These may be used on their own, or two or more may be used together.

This saturated hydrocarbon oligomer has good compatibility with the saturated hydrocarbon polymer (A) (sic) and can be mixed therewith in any proportions. The amount employed may be suitably adjusted according to the desired viscosity of the composition and the type of oligomer used. However, normally, from 1 to 1000 parts (parts by weight; so too below) per 100 parts of the (a) component is preferred, and from 10 to 150 parts is still further preferred. If the amount employed is less than 1 part, then it is not possible to sufficiently reduce the viscosity of the composition and so it is not possible to bring about a sufficient improvement in usability. Furthermore, it is not possible to achieve a sufficient enhancement in the

elongation properties of the cured material, or a sufficient reduction in elastic modulus or enhancement in strength. Again, with more than 1000 parts, problems tend to arise such as a lowering of the curability of the composition, a reduction in the elongation properties, strength and heat resistance of the cured material, or a tendency for bleed-out to occur.

These saturated hydrocarbon oligomers may also be used instead of solvent for the purposes of adjusting the reaction temperature or adjusting the viscosity of the reaction system, at the time of the introduction of the reactive silicon groups into the saturated hydrocarbon polymer.

The curable composition of the present invention contains the (a) component which possesses room temperature curability and provides a cured material which has good elongation properties and strength and also good water resistance, heat resistance, weather resistance and moist air barrier properties, together with the (b) component which has good compatibility with the (a) component, which does not readily bleed-out and can be mixed therewith in any proportions, and which can be used to readily adjust the viscosity of the composition and, furthermore, it can improve the strength and elongation properties of the cured material without lowering the water resistance, heat resistance, weather resistance and moist air barrier properties derived from the (a) component. Hence, when compared to a composition comprising a conventional rubbery polymer such as an oxyalkylene type polymer, there can be obtained a composition with excellent practical characteristics which provides a cured material of

extremely good weather resistance, heat resistance, moist air barrier properties and water resistance, and with little bleed-out. Moreover, the composition of the present invention which is obtained shows excellent usability when employed in practice and, in the case where used as a sealant, there are few problems in that paint contamination is reduced, etc. The composition can be favourably employed for adhesives and pressure-sensitive adhesives (self-adhesives), paints, sealants for laminated glass and other such sealing agents, waterproofing agents, spray agents, release materials, cast moulded rubber materials and the like.

A curing catalyst may optionally be employed for improving the curing properties of the composition of the present invention. Specific examples of such curing catalysts are silanol condensation catalysts like titanate esters such as tetrabutyl titanate and tetrapropyl titanate; carboxylic acid tin salts such as dibutyltin dilaurate, dibutyltin maleate, dibutyltin diacetate, tin octylate and tin naphthenate; the reaction products of dibutyltin oxide and phthalate esters; dibutyltin diacetylacetonate; organo-aluminium compounds such as aluminium tris-acetylacetonate, aluminium tris-ethylacetoacetate and diisopropoxyaluminium ethylacetoacetate; chelate compounds such as zirconium tetraacetylacetonate and titanium tetraacetylacetonate; lead octylate; amine compounds such as butylamine, octylamine, dibutylamine, monoethanolamine, diethanolamine, triethanolamine, diethylenetriamine, triethylenetetramine, oleylamine, cyclohexylamine, benzylamine, diethylaminopropylamine, xylylene diamine, triethylenediamine, guanidine, diphenylguanidine, 2,4,6-tris(dimethylaminomethyl)phenol,

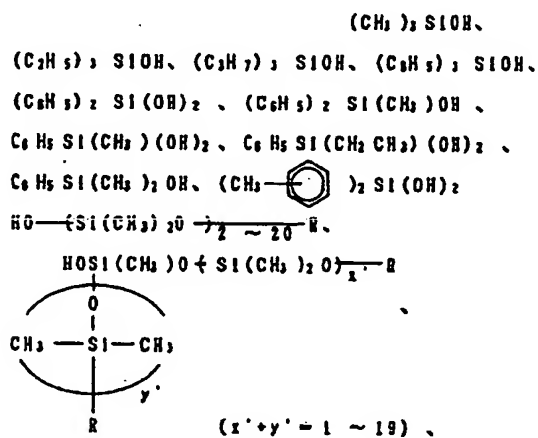
morpholine, N-methylmorpholine, 2-ethyl-4-methylimidazole and 1,8-diazabicyclo(5,4,0)undecene-7 (DBU) or the carboxylic acid salts of these; low molecular weight polyamide resins obtained from excess polyamine and a polybasic acid; the reaction product of excess polyamine and an epoxy compound; a silane coupling agent with an amino group such as γ -aminopropyltrimethoxysilane, N-(β -aminoethyl)aminopropylmethyldimethoxysilane or the like, and also other known silanol condensation catalysts such as acidic catalysts and basic catalysts, etc. These catalysts may be used on their own or two or more may be used together.

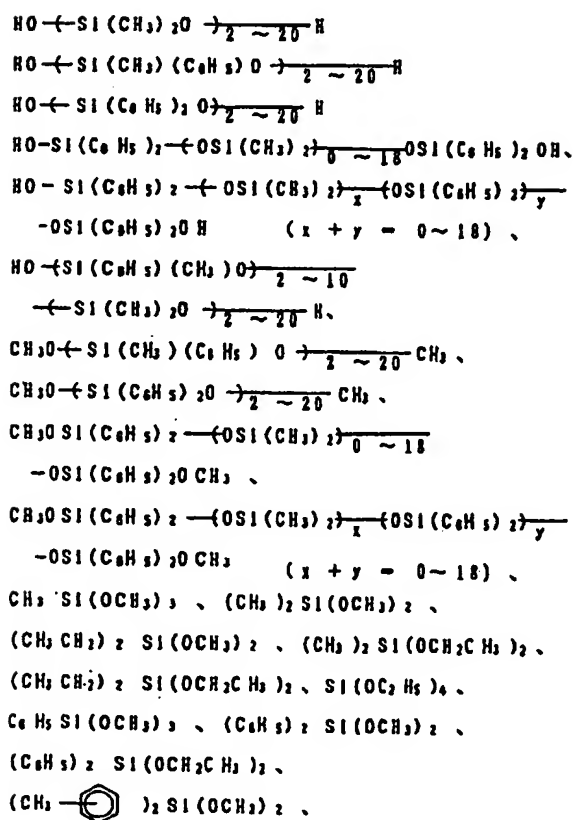
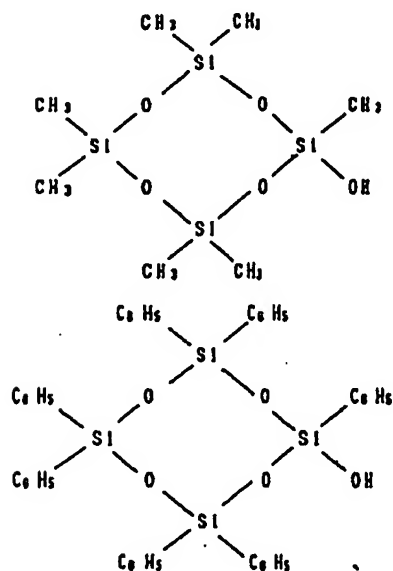
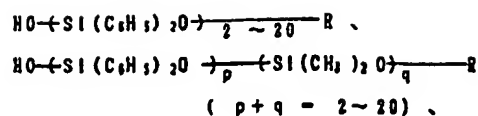
The amount employed in the case where a curing catalyst is used is preferably 0.01 to 50 parts, and more preferably 0.1 to 5 parts, per 100 parts of the (a) component.

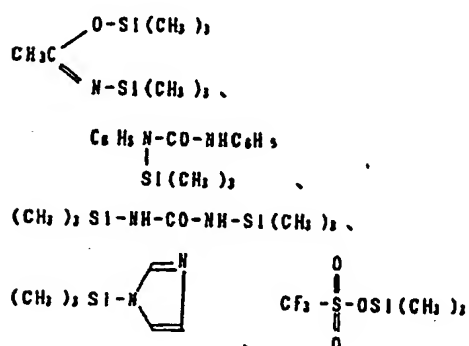
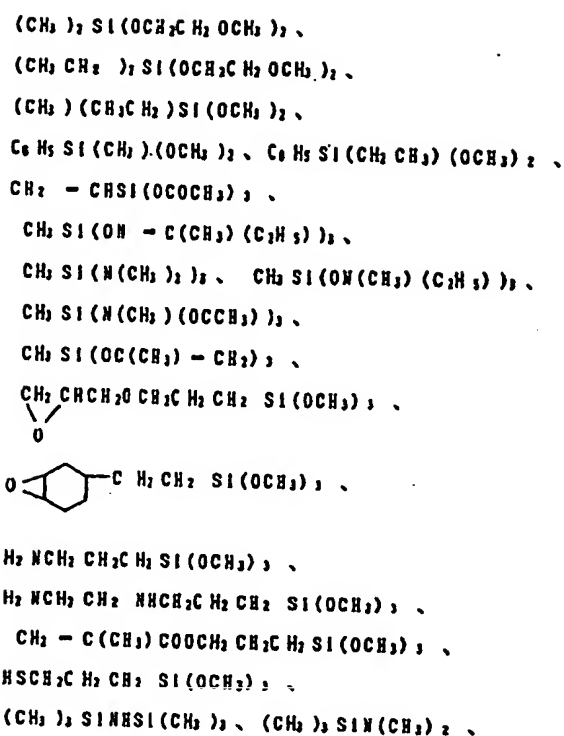
In the composition of the present invention various other additives can optionally be used, such as properties regulators, storage stability improvers, plasticizers other than the aforesaid saturated hydrocarbon oligomer, fillers, adhesion improvers, sulphur type ageing inhibitors, phosphorus type ageing inhibitors and other such generally-used ageing inhibitors, 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), tetrakis[methylene-3(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]methane or other such phenol type radical inhibitors¹, ultraviolet light absorbers such as 2(2'-hydroxy-3',5'-di-tert-butylphenyl)benzotriazole and bis(2,2,6,6-tetramethyl-4-piperidine)sebacate, metal deactivators, ozone degradation preventives, light stabilizers, amine type

radical chain inhibitors, phosphorus type peroxide degrading agents, citric acid, lubricants, pigments, blowing agents or the like.

Specific examples of the aforesaid properties-regulators, which are used for broadly controlling the properties of the cured material such as the strength and elongation, are the following silicon compounds which contain at least one hydrolyzable group or silanol group:-







or the partially-hydrolysed condensates of these silicon compounds, but there is no restriction to the examples given. In the formulae shown, R is a hydrogen atom or a hydrocarbon group with from 1 to 20 carbons.

The amount used in the case where a properties-regulating agent is employed is preferably from 0.01 to 50 parts, and more preferably from 0.1 to 5 parts, per 100 parts of component (a).

Examples of the aforesaid storage stability improvers are compounds with a hydrolyzable group bonded to a silicon atom, and also organic acid ortho esters. As specific examples of the storage stability improvers, there are those compounds with a hydrolyzable group bonded to a silicon atom amongst the aforesaid specific examples of properties-regulators, and also methyl orthoformate. The amount used in the case where a storage stability improving agent is employed is preferably from 0.01 to 50 parts, and more preferably from 0.1 to 5 parts, per 100 parts of component (a).

Where a plasticizer other than the aforesaid saturated hydrocarbon oligomer is also used, there are no particular restrictions thereon and generally-employed plasticizers can be employed but it is preferred that they be compatible with the composition of the present invention. Specific examples of such plasticizers are hydrocarbon compounds like liquid polybutadiene and partially-hydrogenated terphenyl; phthalate esters such as dibutyl phthalate, diheptyl phthalate, di(2-ethylhexyl) phthalate, butyl benzyl phthalate and butyl phthalylbutyl glycolate; non-aromatic dibasic acid esters such as dioctyl adipate and dioctyl sebacate; polyalkylene glycol esters such as diethylene glycol benzoate and triethylene glycol dibenzoate; and phosphate esters such as tricresyl phosphate and tributyl phosphate. These may be used on their own or two or more can be used together.

The amount used in the case where an aforesaid plasticizer is employed is preferably from 0.1 to 500

parts, and more preferably from 10 to 100 parts, per 100 parts of component (a).

Specific examples of the aforementioned fillers are wood flour, pulp, cottonⁱⁱ, asbestos, glass fibre, carbon fibre, mica, walnut shell flour, rice hull flour, graphite, diatomaceous earth, white clay, fumed silica, precipitated silica, anhydrous silicic acid, carbon black, calcium carbonate, clay, talc, titanium dioxide, magnesium carbonate, quartz, microfine aluminium powder, flint powder, zinc powder or the like. Of these fillers, the thixotropic fillers such as precipitated silica, fumed silica and carbon black, and also calcium carbonate, titanium dioxide and talc, etc, are preferred. The amount used in the case where a filler is employed is preferably from 1 to 1000 parts, and more preferably from 50 to 200 parts, per 100 parts of component (a).

As the aforesaid adhesion-improving agent, there can be employed a generally-used adhesive, a silane coupling agent such as an aminosilane compound or an epoxysilane compound, or other such compounds. Specific examples of the adhesion-improving agent are phenolic resins, epoxy resins, γ -aminopropyltrimethoxysilane, N-(β -aminoethyl)aminopropylmethyldimethoxysilane, coumarone-indene resins, rosin ester resins, terpene-phenol resins, α -methylstyrene/vinyltoluene copolymer, polyethylmethylstyrene, alkyl titanates and aromatic polyisocyanates. The amount used in the case where an adhesion-improving agent is employed is preferably from 0.01 to 50 parts, and more preferably from 0.1 to 5 parts, per 100 parts of component (a).

Examples of the aforesaid sulphur type ageing inhibitors are mercaptans, mercaptan salts, sulphides including sulphide carboxylic acid esters and hindered phenol type sulphides, polysulphides, dithiocarboxylic acid salts, thioureas, thiophosphates, sulphonium compounds, thioaldehydes, thioketones, mercaptals, mercaptols, monothioacids, polythioacids, thioamides and sulfoxides. Specific examples of these sulphur type ageing inhibitors are 2-mercaptobenzothiazole which is a mercaptan; 2-mercaptobenzothiazole zinc which is a mercaptan salt; 4,4'-thio-bis(3-methyl-6-tert-butylphenol), 4,4'-thio-bis(2-methyl-6-tert-butylphenol), 2,2'-thio-bis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)sulphide, terephthaloyl di(2,6-di-methyl-4-tert-butyl-3-hydroxybenzyl)sulphide, phenothiazine, 2,2'-thio-bis(4-octylphenol) nickel, dilauryl thiodipropionate, distearyl thiodipropionate, dimyristyl thiodipropionate, ditridecyl thiodipropionate, distearyl β,β' -thiodibutyrate, lauryl-stearyl thiodipropionate and 2,2-thio[diethyl-bis-3(3,5-di-tert-butyl-4-hydroxyphenol)propionate] which are sulphides; 2-benzothiazole disulphide which is a polysulphide; zinc dibutyl dithiocarbamate, zinc diethyl dithiocarbamate, nickel dibutyl dithiocarbamate, zinc di-n-butyl dithiocarbamate, dibutylammonium dibutyl dithiocarbamate, zinc ethyl-phenyl-dithiocarbamate and zinc dimethylcarbamate which are dithiocarboxylic acid salts; 1-butyl-3-oxy-diethylene-2-thiourea, di-o-tolyl-thiourea and ethylene thiourea which are thioureas; trilauryl trithiophosphate which is a thiophosphate, and the like. When compared to other ageing inhibitors, when a sulphur type ageing inhibitor of the kind described above is used in the composition of the present invention, it is

possible to markedly prevent decomposition and degradation of the main chain by heat, and it is possible to prevent surface tack (stickiness). The amount used in the case where an aforesaid sulphur type ageing inhibitor is employed is preferably from 0.01 to 50 parts, and more preferably from 0.1 to 5 parts, per 100 parts of component (a).

Next, the curable composition of the present invention is explained in further detail based on examples.

Production Example 1

40 g of isobutylene polymer of molecular weight about 5,000 having isopropenyl groups at about 92% of the two terminals, and 2 g of toluene were weighed out into a 100 ml four-necked flask and then deaerated under reduced pressure for 2 hours at 90°C. Next, under a nitrogen atmosphere, 21.7 μ l of chloroplatinic acid catalyst solution (a 0.066 mol/litre isopropyl alcohol/tetrahydrofuran {1/2 volume ratio} solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was added at room temperature, after which heating and stirring were carried out for a while and then the mixture returned to room temperature and 2.47 g of methyldichlorosilane added, following which reaction was carried out for 16 hours at 90°C.

When the amount of the aforesaid isopropenyl groups remaining in the isobutylene polymer present in the reaction solution was measured quantitatively by an IR spectroscopy method, it was found that practically none remained.

Next, 4.7 ml of methyl orthoformate and 1.7 ml of methanol were added and reaction carried out for 3 hours at 70°C. The pH of the reaction system at this point was about 7, so it was neutral. The volatile component was eliminated under reduced pressure and then 120 ml of hexane added to the residue and thorough stirring performed. The insoluble materials were removed by filtering. The hexane was distilled off from the filtrate and there was obtained isobutylene polymer with $-\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$ groups at both terminals.

By NMR, it was found that the aforesaid reactive silicon groups had been introduced at about 86% of the molecular terminals.

Production Example 2

176 g of a MeOH solution of NaOCH_3 (concentration 28%) was added to 800 g of hydroxy-terminated hydrogenated butadiene (Polyether HA, produced by the Mitsubishi Kasei Corporation) and an oxymetallizing reaction carried out while removing volatiles at 130°C (about 5 hours). Subsequently, 99.1 g of 3-chloro-2-methyl-1-propene was added and reaction carried out for 3 hours at 90°C, after which purification was performed.

When the liquid polymer obtained was analysed by the NMR method and GPC method, it was found to be polymer of average molecular weight 3500 which had isopropenyl groups introduced at 76% of the total terminals.

Using 40 g of this polymer of average molecular weight 3500 and 13.5 μl of chloroplatinic acid (a 0.2 mol/litre isopropyl alcohol solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), together

with 4.6 g of methyldichlorosilane, reaction was carried out for 8 hours at 85°C in the same way as in Production Example 1, after which 8.7 ml of methyl orthoformate and 3.2 ml of methanol were added and reaction carried out for 3 hours at 70°C.

When the amount of residual isopropenyl groups in the reaction solution was determined quantitatively by IR spectroscopy, essentially no such groups were found to be present. Again, when the amount of reactive silicon groups was determined by NMR, it was found that essentially 100% of the terminal isopropenyl groups had formed $(\text{CH}_3\text{O})_2\text{Si}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-$ groups.

Production Example 3

320 g of polyoxypropylene glycol of average molecular weight 3200 (PP-4000 produced by Sanyo Chemical Industries) was introduced into a 1 litre pressure-resistant autoclave which had been purged with nitrogen, then 40.8 g of NaOH powder (purity 98%) added, after which the temperature was raised to 60°C and stirring carried out for 1 hour. Next, 7.76 g of bromochloromethane was added and stirring carried out for 10 hours while still at 60°C, after which 9.2 g of allyl chloride was added and reaction carried out for a further 10 hours. After cooling, the contents were removed and transferred to an 8 litre separable flask. 1.5 litres of n-hexane was added to this and stirring carried out until uniform, after which 1.5 litres of 3% aqueous sulphuric acid was added and stirring carried out for 1 hour. Thereafter, the mixture was left to stand for 1 hour and separation took place into two layers, a transparent hexane layer and an aqueous layer.

The pH of the aqueous layer at this time was less than 6. The hexane layer was separated off and then the n-hexane driven off by means of an evaporator. A polyether of average molecular weight 8,000 in which 94% of the terminals had been converted to allyl ether groups was obtained.

300 g of the allyl-terminated polyether obtained was placed in a 1 litre pressure-resistant autoclave which had been purged with nitrogen, then 0.3 g of a 10% isopropyl alcohol solution of chloroplatinic acid added and a uniform mixture formed, after which 6.0 g of methyldimethoxyhydrosilane was added. The temperature was then raised to 90°C after which stirring was carried out for 4 hours.

When analysis was carried out by GLC, it was confirmed that practically the entire amount of the silane introduced had reacted with the allyl groups at the polyether terminals, and a terminal silyl-modified polyether produced.

Examples 1 to 5 and Comparative Examples 1 and 2

Components (a) and (b) and the other components shown in Table 1 were mixed together and then subjected to kneading on a triple roll mill, to prepare a uniform composition. In Examples 1 to 5, the viscosity of the composition was lowered by the addition of the polybutene, and the usability of the composition thereby enhanced.

A sheet of thickness about 3 mm was prepared from each of the aforesaid components and curing carried out for 4

days at room temperature and for a further 4 days at 50°C. When the surface state of the cured material was observed, no bleeding at all was noted. Next, the heat resistance and the weather resistance (weatherability) of the cured materials were evaluated. The results are shown in Table 1.

The polybutene in Table 1 was Polybutene OH produced by the Idemitsu Petrochemical Co., the ageing inhibitor in the evaluation of the heat resistance was dilauryl thiodipropionate and in the evaluation of weatherability it was 2(2'-hydroxy-3',5'-di-tert-butylphenyl)-benzotriazole.

Table 1

Example Number →			1	2	3	4	5	Comp.1	Comp.2
Composition (parts)	component (a)	polymer obtained in Production Example 1	100	100	100	-	-	-	-
		polymer obtained in Production Example 2	-	-	-	100	100	-	-
		polymer obtained in Production Example 2	-	-	-	-	-	100	100
	component (b)	polybutene	40	50	60	40	50	-	-
		DOP	-	-	-	-	-	40	50
	CaCO ₃		100	100	100	100	100	100	100
	tin octylate		3	3	3	3	3	3	3
	laurylamine		0.75	0.75	0.75	0.75	0.75	0.75	0.75
	ageing inhibitor		1	1	1	1	1	1	1
Results of the Evaluations	Heat Resistance*		>300	>300	>300	>300	>300	0.1	0.1
	Weatherability**		>5000	>5000	>5000	>5000	>5000	200	200

Key: * time (days) for the surface to become matt
** time (days) for the surface to become matt

Key:

* time (days) for the surface to begin to melt at 130°C

** time (hours) for the surface to begin to melt in a sunshine weathermeter test

From the results in Table 1 it can be seen that in the systems employing saturated hydrocarbon polymer (A) (sic) and saturated hydrocarbon oligomer, extremely high heat resistance and weather resistance are shown.

[Effects of the Invention]

The curable composition of the present invention has a low viscosity and good usability, and it produces a high-strength high-elongation cured material which shows little bleeding and outstanding heat resistance, water resistance, adhesion properties and weatherability, etc.

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 (plus 1 other)

Translator's Notes

ⁱ Perhaps here and later in this same paragraph, the Japanese original should refer to radical 'terminators' rather than 'inhibitors'.

ⁱⁱ The Japanese actually says 'cotton chip' but it is not clear what is meant.